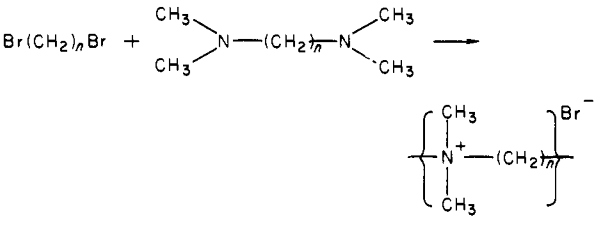
to that found for typical dialkylammonium vesicles.[12,13]

Our second approach to the polymeric vesicle is the use of ionene polymers **7** prepared according to eq 1.[14]



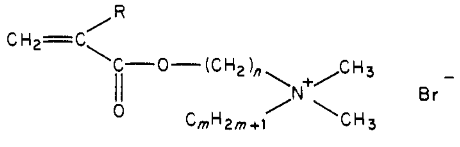
(1)

7 (n = 12, 16, 20)

Polymer **7** gave clear dispersions upon sonication. Electron microscopy indicated that vesicles are formed from **7** (n = 12, 20) and that vesicles and lamellae are present for aqueous **7** (n = 16). An electron micrograph of aqueous **7** (n = 20) is shown in Figure 1b. The observed layer width (ca. 25 Å) is consistent with the membrane formation by chain folding as illustrated in Figure 2b.

The polymer membranes of **7** undergo phase transition: T_c = 53 °C for n = 20, T_c = 27 °C for n = 16, and no transition detected for n = 12. The molecular weight of aqueous **7** (n = 20) was 2×10^6. As anticipated, ionene polymers composed of alkyl chains of different lengths do not form the membrane structure.

In our previous attempts mentioned above, we prepared amphiphilic monomers **8** and examined their polymerization behavior in water and the change in the aggregate morphology due to polymerization.[4,5,16]



8a, R = H (n, m = 10, 12; 10, 18; 16, 12; 16, 18)
b, R = CH_3 (n, m = 16, 18)

Unfortunately, the bilayer structure was not clearly seen by electron microscopy for the monomer aggregate and the polymerized aggregate. The T_c value of the aqueous aggregate lowered appreciably upon polymerization: T_c = 61 °C for **8a** (n, m = 16, 18) monomer and 31 °C upon polymerization; T_c = 46 °C for **8b** (n, m = 16, 18) monomer and 31 °C upon polymerization. These results suggest that polymerization promotes disorder in the bilayer assemblage.

Recently, Regen and co-workers[17] reported vesicle formation from **8b** (n, m = 11, 16) and its polymer, but the bilayer structure was not clearly visibile by electron microscopy. Attempts to stabilize bilayer vesicles by polymerization were also reported by Ringsdorf et al.,[18] Chapman et al.,[19] and O'Brien et al.[20] They synthesized dialkyl amphiphiles with the diacetylene moiety in the center of the alkyl chain. The polymerized vesicle showed enhanced stability, although the phase transition behavior was lost upon polymerization.

In conclusion, we could show that vinyl polymers with the hydrophilic main chain can form bilayer vesicles through the side-chain aggregation. The vesicle retains the liquid crystalline characteristics. This is important, since the peculiar property of the bilayer membrane is related to its liquid crystalline nature. The enhanced stability of polymer vesicles **1–7** is now under detailed investigation. For example, these vesicles undergo fusion less efficiently than ordinary bilayer vesicles. Our interests are directed to the use of the polymer vesicle as models of the vesicle–protein interaction and the vesicle–cell interaction and as carriers of drugs and other biologically active substances into the cell.

Acknowledgment. We are grateful to Professor M. Takayanagi for the use of an electron microscope (Hitachi, H-500). This research was partially supported by Grant-in-Aid (447079) for Scientific Research, Ministry of Education.

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[14] Ionene polymers were prepared according to the procedure of Rembaum and Noguchi.[15] A typical procedure is as follows: 2.64 g (6×10^{-3} mol) of 1,20-dibromoeicosane and 2.21 g (6×10^{-3} mol) of 1,20-bis(N,N-dimethylamino)eicosane were dissolved in 20 mL of purified tetrahydrofuran (THF) and stirred for 100 h at room temperature. The precipitates were washed with THF and reprecipitated from dimethyl sulfoxide and THF to give **7** as a colorless powder (n = 20) in 2.8 g (58%) yield.

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[16] Polymerization condition: monomer 10 mM in water; 11 °C; dose rate (^{60}Co) 9.5×10^4 R/h.

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Nucleophilic Oxygen Atom Transfer Reactions by Persulfoxide and Persulfone[1]

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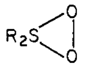
Oxygen atom transfer reactions are of current interest as a model of monooxygenase enzymes;[2] among them are those from carbonyl oxides,[3] pyridine N-oxide,[4] and unstable cyclic peroxides.[5] Especially, much attention has been concentrated on the structure[6] and reactions[3,7] of carbonyl oxides. In the course of studies on the photooxidation of benzoins[8] and diazoketones,[9] we could characterize a nucleophilic O-transfer reaction by intermediates formed in the sensitized photooxidation of sulfides and sulfoxides.

Foote et al.[10] have elegantly suggested that in the reaction of sulfide R_2S with $^1O_2$, a persulfoxide structure **1** is more appropriate than diradical **2** or cyclic dioxirane one **3** as an intermediate oxidizing another sulfide molecule to sulfoxide. Their rationale

$R_2S^+OO^-$ 1

$R_2\dot{S}O\dot{O}$ 2



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is based on the trapping of the intermediate by Ph_2S and the dramatic acceleration of the photooxidation of R_2S by protic

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[1] Contribution No. 287.

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[3] (a) H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966); (b) G. A. Hamilton and J. R. Giacin, *J. Am. Chem. Soc.*, **88**, 1584 (1966); (c) T. A. Hinrichs, V. Ramachandren, and R. W. Murray, *ibid.*, **101**, 1282 (1979); (d) W. Ando, H. Miyazaki, and S. Kohmoto, *Tetrahedron Lett.*, 1317 (1979).

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Table I. Relative Photooxidation of Dimethyl Sulfide and Sulfoxide[a]

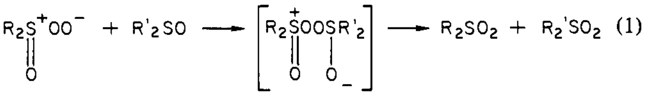
substrate	solvent[b]	relative rate[c]	Dabco effect[d]
Me_2S	PhH	(1.00)	no (1.0)
	MeOH-PhH	19	no (25)
Me_2SO	PhH	0.021	yes (0.004)
	MeOH-PhH	0.0042	yes (0.002)

[a] Photooxidation of 0.05 M Me_2S or 1 M Me_2SO under O_2 in the presence of 0.05 mM TPP; irradiated at over 400 nm for 0.5-2 h at 20 °C using a medium-pressure Hg lamp. [b] MeOH-PhH means a 1:1 mixture by volume. [c] Relative rates were determined by using a merry-go-round apparatus and the GLC analyses of products; average of two or three determinations. [d] Dabco effect was determined from the relative rates, which are shown in parentheses, in the presence of 0.5 mM Dabco.

solvents. Since then zwitterionic **1** has been noted in the reaction of various sulfides with $^1O_2$,[11] but its reactivity is not thoroughly clarified.

When irradiated under oxygen in the presence of *meso*-tetraphenylporphine (TPP), the photooxidation of dimethyl sulfoxide (Me_2SO) was much slower than that of dimethyl sulfide (Me_2S), as reported previously.[12] The relative rates in Table I reveal that the photooxidation of Me_2SO is significantly retarded by methanol, which is in sharp contrast to the sulfide case. Here it is apparent that the photooxidation of Me_2SO proceeds via $^1O_2$, since the reaction is slowed down by 1,4-diazabicyclo[2.2.2]octane (Dabco).[13,14]

The two contrasting solvent effects led us to assume a nucleophilic O transfer by intermediary persulfone **4** (eq 1), since similar nucleophilic oxidation of sulfoxides by peroxide anions is known[16] and presumably retarded by protic solvents.[17]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(1)

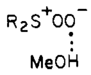
Actually, the assumption was ascertained by the relative reactivities of sulfides and sulfoxides, which are relatively inert to $^1O_2$, toward the oxidizing intermediates **1** and **4** (Table IIA). The resulting reactivity order of $Ph_2SO \sim Me_2SO \gg Ph_2S$ for **1** and **4** indicates the nucleophilic O transfer to sulfoxides. This order is in sharp contrast to the electrophilic oxidation by peracid: $Ph_2S \gg Me_2SO > Ph_2SO$ (last column in Table II). The substituent effect on diphenyl sulfoxides is also consistent with the nucleophilic O transfer (Table IIB). That is, the positive ρ values of 0.25 and 0.23 for **1** and **4**, respectively, in benzene clearly demonstrate the nucleophilic nature of the O transfer. This is in contrast to the corresponding value of $\rho = -1.06$ for the electrophilic oxidation with perbenzoic acid.

Table II. Relative O-Transfer Reactivities of Persulfoxide and Persulfone

	relative reactivities[a]			
substrate[b]	$Me_2S^+OO^-$ in PhH	$Me_2S^+OO^-$ in MeOH–PhH	$Me_2S^+(O)OO^-$ in PhH	PBA[c] in PhH
	A. Miscellaneous			
$PhMeC{=}CH_2$	~0.03[d]	~0.02[d]	<0.01	0.045
Ph_2S	0.13	0.18	~0.05	86
$(p\text{-}ClPh)_2S$	0.031	0.035		
Me_2SO	1.12	0.84	1.26	8.1
Ph_2SO	(1.00)	(1.00)	(1.00)	(1.00)
	B. Substituted Diphenyl Sulfoxides			
$(p\text{-}MeOPh)_2SO$	0.82	~1.1	0.81	3.64
$(p\text{-}MePh)_2SO$	0.78	0.89	0.88	2.06
Ph_2SO	(1.00)	(1.00)	(1.00)	(1.00)
$(p\text{-}ClPh)_2SO$	1.39	0.83	1.38	0.307
ρ (vs. σ)	0.252	−0.05	0.232	−1.06
(r)[e]	(0.961)	(0.725)[f]	(0.988)	(0.999)

[a] Relative reactivities by competitive reactions with 0.05–0.2 M substrate, 0.05 mM TPP, and 0.1 M Me_2S or 0.5 M Me_2SO in aerated benzene at 20 °C irradiated at over 400 nm. Products were determined by GLC at an early stage (i.e., <10% conversion). [b] Ph = C_6H_5 or C_6H_4. [c] By rate measurements of perbenzoic acid oxidation in benzene at 25 °C. [d] Approximate values from the epoxide yields; the major reaction was C–C cleavage (i.e., acetophenone). [e] Correlation coefficient. [f] Very poor correlation.

On the other hand, the substituent effect for the reaction of **1** with diphenyl sulfoxides in MeOH–PhH was very small and of poor correlation.[18] This may be due either to the hydrogen bonding (**5**)[10] or the methanol adduct (**6**) in which the nucleophilic nature of persulfoxide **1** may be altered. If **6** were the major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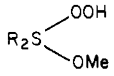
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oxidizing intermediate in the presence of MeOH, the relative reactivity should be parallel to that of the peracid oxidation (i.e., $R_2S \gg R_2SO$) and the ρ value be definitely negative, both of which were not the case. Then the actual oxidizing species in MeOH–PhH is probably **5**. This is also consistent with the fact that the relative reactivities of $R_2SO \gg R_2S$ (as a nucleophilic oxidant) and $Ph_2S > (p\text{-}ClPh)_2S$ (as an electrophilic oxidant) are not altered by solvent MeOH. The corresponding reaction of sulfides with **4** in MeOH–PhH was too low to obtain reliable data.

As to the sulfide oxidation, the reactivity order of $Ph_2S > (p\text{-}ClPh)_2S$ indicates that sulfides are in turn oxidized electrophilically by **1** and **5**.[19] This seems to be derived from the relatively strong nucleophilicity of sulfur atom in sulfides in comparison to that in sulfoxides.[20] The intermediates **1** and **4** are not effective for the epoxidation of olefins, the major reaction for α-methylstyrene being the C–C cleavage affording acetophenone. A small amount (≤1%) of phenol was detected in the photooxidation of Me_2S in benzene. These reactions resemble those of carbonyl oxides[9] and presumably proceed via a radical pathway as a minor reaction.

In conclusion, the intermediate structures are surely persulfoxide **1** and persulfone **4**, since their characteristic reaction is a nucleophilic O transfer to sulfoxide such as eq 1. Less efficient reactions are the electrophilic oxidation of sulfides and the oxidative C–C cleavage of olefins. Finally, the present reactions of **1** are in contrast to the reported reactivity of some persulfoxides, derived from H_2O_2 and Martin's sulfuranes, capable of epoxidizing olefins.[21] We tentatively assume the epoxidation might be due to some other species, e.g., a hydroperoxysulfurane such as **6**.

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[12] G. O. Schenck and C. H. Krauch, *Chem. Ber.*, **96**, 517 (1963).

[13] The apparent no effect of Dabco for the case of dimethyl sulfide only reflects the fact that its reaction with $^1O_2$ is as fast as the quenching by Dabco; C. S. Foote, "Singlet Oxygen", H. H. Wasserman and R. W. Murray, Ed., Academic Press, New York, 1979, p 166.

[14] Dabco may quench any other excited species during the photooxidation. However, under the irradiation conditions of Table I, the reaction of R_2S was not affected by the addition of Dabco, which suggests that no quenching of excited dyes by Dabco occurs. Hence, the observed retarding effect of Dabco on the reaction of Me_2SO should be due to the quenching of $^1O_2$. Another possibility such as the electron-transfer photooxidation[15] is also untenable because of the smooth reaction in nonpolar solvents.

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[17] In fact, the oxidation of sulfoxide by *t*-BuOO⁻ is possible only in aprotic solvents.[16c,d]

[18] The low coefficient of $r = 0.725$ means a very poor correlation.

[19] Recently, a negative ρ value (i.e., $\rho = -0.32$ vs. σ) has been reported for the reaction of **1** (R = Et) with diphenyl sulfides.[11e]

[20] Sulfides are often used to reduce many types of peroxides.

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